

Normal-mode analysis of the structures of perovskites with tilted octahedra

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An analysis of the normal modes of vibration of a cubic perovskite that have condensed to produce phases with tilted octahedra is presented. Only structures with octahedral tilts that double a repeat distance are considered; these involve small rotations of the octahedra about pseudocubic (100) directions. Phases with more than one octahedral tilt often possess atomic displacements in addition to those associated directly with the tilts. A Landau potential has been constructed which includes all parameters needed to describe the low-symmetry phases. In addition to the spontaneous macrostrain, seven different order parameters are required to describe the possible transitions between phases with only one type of *A* and one type of *B* cation. Arguments based on the Landau expansion suggest that structural displacements associated with some of these order parameters are unlikely to be present, and that some subsets of displacements may have a higher symmetry than required by the space group of the lower-symmetry phase. Comparison is made between these predictions and reported structural refinements. Where relevant, phases with more than one type of *A* or more than one type of *B* cation are considered.

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1. Introduction

The high-temperature cubic phase – the aristotype (Megaw, 1973) – is taken to have the following fractional atomic coordinates:

$$\begin{aligned} A & \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right) \\ B & (000) \\ \text{OI} & (00\frac{1}{2}) \\ \text{OII} & (0\frac{1}{2}0) \\ \text{OIII} & (\frac{1}{2}00). \end{aligned}$$

The numbering of the anions (not necessarily O atoms) follows the convention adopted by Cowley (1964). After a displacive phase transition, the topology of the structure is unchanged but some of the atoms are displaced from the positions of high symmetry that they occupy in the aristotype. These phases with lower symmetry will be called hettotypes (Megaw, 1973). Cochran & Zia (1968) point out that the displacements can be analysed in terms of normal modes of the aristotype. We use Cowley's labelling convention so that the condensed modes can be readily identified with the irreducible representations and wavevectors of the normal modes of the aristotype listed in the Appendix of Cowley's paper. (Cowley describes the structure with *A* at the origin, but this difference is irrelevant.)

The hettotypes considered here involve tilting of the octahedra caused by condensation of modes with wavevectors at the *R*- and *M*-points of the cubic Brillouin zone. These points,

$[2\pi(\frac{1}{2}\frac{1}{2}\frac{1}{2})/a]$ and $[2\pi(0\frac{1}{2}\frac{1}{2})/a]$, respectively, referred to by ζ hereafter with $\mathbf{q} = [2\pi\zeta/a]$, lie on the zone boundary. Possible structures with octahedra tilted by these modes were considered by Glazer (1972), who concluded, from geometrical arguments, that there are 23 such tilt systems (including the aristotype which has no tilts). Only structures with a single type of *A* cation and single type of *B* cation were analysed. In Glazer's notation, an octahedral tilt with $\zeta = (0\frac{1}{2}\frac{1}{2})$ is described by a plus sign, and $\zeta = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ by a minus sign. Equality between different pseudocubic components of the tilt is indicated by using the same letter of the alphabet. Thus, for example, $[a^+a^+a^+]$ describes a hettotype with three tilts of equal angle, with $\zeta = (0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}0\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}0)$; $[a^-a^-c^+]$ describes a structure with two equal tilts with $\zeta = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ but the third tilt, with $\zeta = (\frac{1}{2}\frac{1}{2}0)$, has a different magnitude of tilt angle. Using Cowley's table, a plus tilt about $[001]_{pc}$, for example, corresponds to the normal mode of the aristotype described as

$$[(\frac{1}{2}\frac{1}{2}0), M_3] \quad \text{with} \quad \text{OII}(x) = -\text{OIII}(y),$$

while a minus tilt about $[100]_{pc}$ corresponds to

$$[(\frac{1}{2}\frac{1}{2}\frac{1}{2}), \Gamma_{25}] \quad \text{with} \quad \text{OI}(y) = -\text{OII}(z).$$

The mode in the cubic phase at the *M*-point is a singlet; at the *R*-point it is a triplet.

Glazer included in his list systems such as $[a^-a^-a^+]$. Since the plus and minus tilts correspond to normal modes of the cubic phase that are not related by symmetry, equality in their magnitude can only occur by accident and so such structures

will not be considered. Therefore, only nine possible tilt systems remain – ten including the aristotype.

The nine hettotypes with single types of *A* and *B* cations are listed in Table 1. In the table, each phase is identified using the notation developed by Glazer (1972) and in the third column by one that is useful in constructing a Landau expansion. In the latter description, the pseudocubic component of a plus tilt is described by M_i ($i = 1, 2, 3$), and a minus tilt by R_i ($i = 1, 2, 3$).

The multiplicities of the pseudocubic unit cell, m_i , are defined as

$$a_{pc} = m_1 a_c, \quad b_{pc} = m_2 a_c, \quad c_{pc} = m_3 a_c,$$

where a_c is the value of the cubic lattice parameter extrapolated to the relevant temperature. For the hettotypes considered, m_i equals either 1 or 2. These are given in Table 1 along with the size of the conventional cell.

The space groups for phases with indistinguishable *B* cations are given in column 6. The space group is in the orientation displayed in *International Tables for Crystallography* (1992). The symbols in the second and third columns of Table 1 give non-zero values for the tilt components that correspond to this orientation.

Glazer's original allocation of *Pmmn* for hettotype 8, $[a^+ a^+ c^-]$, is now not generally accepted – there is no reason for equality of the two plus tilts using this space group. Following Leinenweber & Parise (1995), space group $P4_2/nmc$ is used. In this group, there are three crystallographically distinguishable *A* cations [see Woodward (1997a) for a discussion concerning allocation of space groups].

2. Primary and secondary order parameters

Displacements caused by the condensation of a normal mode of the cubic phase form the bases of the primary order parameters. These will be assumed to be the plus and minus tilts at the *M*- and *R*-points of the Brillouin zone in all the materials considered here. The space group that describes a hettotype often allows atomic displacements in addition to those associated directly with the octahedral tilts. Both anions and *A* cations can be involved. The additional displacements form the bases of so-called secondary order parameters. The spontaneous macrostrains that describe the change in shape and size of the pseudocubic unit cell of the hettotypes considered here are also secondary order parameters. Generally, these modes are not soft. Landau theory applied to these phase transitions shows that non-zero values

Table 1
The nine hettotypes.

| Number | +/- notation | $[M_i R_j]$ | Multiplicity | True unit cell | Space group |
|--------|---------------|-------------------|-----------------------|-----------------------------------------|---------------------------------|
| 1 | $a^0 a^0 c^-$ | R_3 | $2 \times 2 \times 2$ | $2^{1/2} \times 2^{1/2} \times 2$ | <i>I4/mcm</i> (140) |
| 2 | $a^- b^0 a^-$ | $R_1 = R_3$ | $2 \times 2 \times 2$ | $2^{1/2} \times 2 \times 2^{1/2}$ | <i>Imma</i> (74) |
| 3 | $a^- a^- a^-$ | $R_1 = R_2 = R_3$ | $2 \times 2 \times 2$ | $2^{1/2} \times 2^{1/2} \times 2^{1/2}$ | <i>R3c</i> (167) |
| 4 | $a^0 a^0 c^+$ | M_3 | $2 \times 2 \times 1$ | $2^{1/2} \times 2^{1/2} \times 1$ | <i>P4/mbm</i> (127) |
| 5 | $a^+ a^+ c^0$ | $M_1 = M_2$ | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | <i>I4/mmm</i> (139) |
| 6 | $a^+ a^+ a^+$ | $M_1 = M_2 = M_3$ | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | <i>Im</i> (204) |
| 7 | $a^0 b^- c^+$ | R_2, M_3 | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | <i>Cmcm</i> (63) |
| 8 | $a^+ a^+ c^-$ | $M_1 = M_2, R_3$ | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | <i>P4₂/nmc</i> (137) |
| 9 | $a^- b^+ a^-$ | $R_1 = R_3, M_2$ | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | <i>Pnma</i> (62) |

Table 2

Atomic displacements in the seven normal modes, the symbol used in the construction of the Landau potential, and character of each mode.

| Normal mode | Displacement | Symbol | Character |
|--------------------------------------------------------|-------------------|-----------|-----------------------------|
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{25}$ | OI(y) = -OII(z) | R_1 | Octahedral minus tilt |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{25}$ | OI(x) = -OIII(z) | R_2 | Octahedral minus tilt |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{25}$ | OII(x) = -OIII(y) | R_3 | Octahedral minus tilt |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | OI(y) = OII(z) | G_{O1} | Octahedral minus distortion |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | OI(x) = OIII(z) | G_{O2} | Octahedral minus distortion |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | OII(x) = OIII(y) | G_{O3} | Octahedral minus distortion |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | A(x) | G_{A1} | A cation displacement |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | A(y) | G_{A2} | A cation displacement |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | A(z) | G_{A3} | A cation displacement |
| $(0, \frac{1}{2}, \frac{1}{2}), M_3$ | OI(y) = -OII(z) | M_1 | Octahedral plus tilt |
| $(\frac{1}{2}, 0, \frac{1}{2}), M_3$ | OI(x) = -OIII(z) | M_2 | Octahedral plus tilt |
| $(\frac{1}{2}, \frac{1}{2}, 0), M_3$ | OII(x) = -OIII(y) | M_3 | Octahedral plus tilt |
| $(0, \frac{1}{2}, \frac{1}{2}), M_1$ | OI(y) = OII(z) | H_1 | Octahedral plus distortion |
| $(\frac{1}{2}, 0, \frac{1}{2}), M_1$ | OI(x) = OIII(z) | H_2 | Octahedral plus distortion |
| $(\frac{1}{2}, \frac{1}{2}, 0), M_1$ | OII(x) = OIII(y) | H_3 | Octahedral plus distortion |
| $(\frac{1}{2}, 0, 0), M_5'$ | OIII(y) | X_{O12} | Octahedral distortion |
| $(\frac{1}{2}, 0, 0), M_5'$ | OIII(z) | X_{O13} | Octahedral distortion |
| $(0, \frac{1}{2}, 0), M_5'$ | OII(z) | X_{O23} | Octahedral distortion |
| $(0, \frac{1}{2}, 0), M_5'$ | OII(x) | X_{O21} | Octahedral distortion |
| $(0, 0, \frac{1}{2}), M_5'$ | OI(x) | X_{O31} | Octahedral distortion |
| $(0, 0, \frac{1}{2}), M_5'$ | OI(y) | X_{O32} | Octahedral distortion |
| $(\frac{1}{2}, 0, 0), M_5'$ | A(y) | X_{A12} | Cation displacement |
| $(\frac{1}{2}, 0, 0), M_5'$ | A(z) | X_{A13} | Cation displacement |
| $(0, \frac{1}{2}, 0), M_5'$ | A(z) | X_{A23} | Cation displacement |
| $(0, \frac{1}{2}, 0), M_5'$ | A(x) | X_{A21} | Cation displacement |
| $(0, 0, \frac{1}{2}), M_5'$ | A(x) | X_{A31} | Cation displacement |
| $(0, 0, \frac{1}{2}), M_5'$ | A(y) | X_{A32} | Cation displacement |

of secondary order parameters arise through terms coupling them to a primary order parameter. This is dealt with in §5.

The primary and secondary order parameters, excluding the macrostrains, found in the nine hettotypes with only one type of *A* and *B* cations, are given in Table 2. In addition, they are identified by a symbol that is used in the construction of the Landau expansion. All are transverse modes of vibration in the aristotype. The notation is self-explanatory except perhaps that for parameter *X* where the middle suffix is used to indicate the wavevector of the condensed mode, while the third suffix gives the direction of displacement of the atoms in that mode.

Table 3

The space group, possible condensed modes and non-zero pseudocubic spontaneous macrostrain in the nine hettotypes.

| Number | Space group | Allowed modes | Macrostrain |
|--------|-------------------|-----------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| 1 | $I4/mcm$ (140) | R_3 | $\varepsilon_{11} = \varepsilon_{22}; \varepsilon_{33}$ |
| 2 | $Imma$ (74) | $R_1 = R_3$ $G_{O1} = G_{O3}$ $G_{A1} = G_{A3}$ | $\varepsilon_{11} = \varepsilon_{33}; \varepsilon_{22}; \varepsilon_{31}$ |
| 3 | $R\bar{3}c$ (167) | $R_1 = R_2 = R_3$ | $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}; \varepsilon_{23} = \varepsilon_{31} = \varepsilon_{12}$ |
| 4 | $P4/mbm$ (127) | M_3 | $\varepsilon_{11} = \varepsilon_{22}; \varepsilon_{33}$ |
| 5 | $I4/mmm$ (139) | $M_1 = M_2$ $H_1 = H_2 \neq H_3$ | $\varepsilon_{11} = \varepsilon_{22}; \varepsilon_{33}$ |
| 6 | $Im\bar{3}$ (204) | $M_1 = M_2 = M_3$ $H_1 = H_2 = H_3$ | $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$ |
| 7 | $Cmcm$ (63) | R_2 M_3 G_{O2} G_{A2} H_3 X_{O32} X_{A32} | $\varepsilon_{11}; \varepsilon_{22}; \varepsilon_{33}$ |
| 8 | $P4_2/nmc$ (137) | R_3 $M_1 = M_2$ G_{O3} $H_1 = H_2$ $X_{O13} = X_{O23}$ $X_{A13} = X_{A23}$ | $\varepsilon_{11} = \varepsilon_{22}; \varepsilon_{33}$ |
| 9 | $Pnma$ (62) | $R_1 = R_3$ M_2 $G_{O1} = G_{O3}$ $G_{A1} = G_{A3}$ H_2 $X_{O21} = X_{O23}$ $X_{A21} = X_{A23}$ | $\varepsilon_{11} = \varepsilon_{33}; \varepsilon_{22}; \varepsilon_{31}$ |

3. Hettotypes with distinguishable A and B cations

Glazer considered phases with a single type of A cation and a single type of B cation. However, there is clear evidence that in BaBiO₃ there is ordering of the valency on the bismuth ions, and the material would be better described as Ba₂Bi^{III}Bi^VO₆ (Cox & Sleight, 1979). In such phases, the symmetry per formula unit is less than in the corresponding phase with identical B cations, and the relevant space group is a subgroup of the space group that describes the hettotype with identical B cations.

A number of perovskites possess distinguishable A cations. An example is CaFeTi₂O₆ with tilt system [$a^+a^+c^-$], which crystallizes in space group $P4_2/nmc$ (Leinenweber & Parise, 1995). The space group provides three distinct sites for the A cations; Fe ions occupy two of them, neither of which allow any displacement, while Ca goes into a site which permits a displacement in the direction of the fourfold axis. No perovskite with identical A cations has been found to possess this tilt system (Woodward, 1997b).

4. Strength of the condensed modes

In Table 3, the condensed modes that may be present in each hettotype are listed. These have been determined by examination of the displacements allowed by the symmetry of the space group.

Following Cochran & Zia (1968), the strength, W , of each condensed mode can be evaluated in terms of the fractional coordinates of the displaced atoms and the relevant lattice parameter. The expression for W is

$$W = (v/v') \sum_{\lambda k} m_k u^2(\lambda k, \mathbf{q}R), \quad (1)$$

where m_k is the mass of atom k , $u(\lambda k, \mathbf{q}R)$ is the displacement of atom k in subcell λ by mode $[\mathbf{q}R]$ acting on its own, v' is the volume of the unit cell of the hettotype, and v is the volume the aristotype would have at the temperature under consideration. Values of W for a number of materials are given in Table 4.

[A listing of the atomic displacements from positions of high symmetry in each hettotype, and an expression for the weight of a condensed mode in terms of these displacements and lattice parameters in each phase can be obtained from the author.]

5. Proposed Landau potential and the number of condensed modes in each hettotype

A Landau expansion involving the seven separate order parameters and macroscopic strain that can reproduce the hettotypes is discussed here. An expression for the excess free energy, F , only to fourth order in the order parameters and including only the lowest-order coupling terms, is of the form

$$F = \frac{1}{2}a_r R_i^2 + \frac{1}{2}b_r R_i^2 R_j^2 + \frac{1}{4}c_r R_i^4 + \frac{1}{2}a_m M_i^2 + \frac{1}{2}b_m M_i^2 M_j^2 + \frac{1}{4}c_m M_i^4 + \frac{1}{2}f_{rm} R_i^2 M_i^2 + \frac{1}{2}g_{rm} R_i^2 M_j^2 + \frac{1}{2}a_g G_i^2 + \frac{1}{2}b_g G_i^2 G_j^2 + \frac{1}{4}c_g G_i^4 + \frac{1}{2}f_{gr} G_i^2 R_i^2 + \frac{1}{2}g_{gr} G_i^2 R_j^2 + \frac{1}{2}a_h H_i^2 + \frac{1}{2}b_h H_i^2 H_j^2 + \frac{1}{4}c_h H_i^4 + \frac{1}{2}f_{hm} H_i^2 M_i^2 + \frac{1}{2}g_{hm} H_i^2 M_j^2 + \frac{1}{2}a_x X_{ij}^2 + \frac{1}{2}b'_x X_{ij}^2 X_{kj}^2 + \frac{1}{2}b''_x X_{ij}^2 X_{ik}^2 + \frac{1}{4}c_x X_{ij}^4 + \frac{1}{2}f_{xrm} X_{ij}^2 R_j^2 M_i^2 + \frac{1}{2}c_{11} \varepsilon_{ii}^2 + c_{12} \varepsilon_{ii} \varepsilon_{jj} + \frac{1}{2}c_{44} \varepsilon_{ij}^2 + \frac{1}{2}f_{er} \varepsilon_{ii} R_i^2 + \frac{1}{2}g_{er} \varepsilon_{ii} R_j^2 + h_{er} \varepsilon_{ij} R_i R_j + \frac{1}{2}f_{em} \varepsilon_{ii} M_i^2 + \frac{1}{2}g_{em} \varepsilon_{ii} M_j^2. \quad (2)$$

G_i and X_{ij} represent two normal modes each, G_{Ai} , G_{Oi} , X_{Aij} and X_{Oij} . The former pair involve displacement of the A cation and one of the anions with $\zeta = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$. Terms involving coupling between the macrostrain, ε_{ij} , and G_i , H_i and X_{ij} are likely to be unimportant compared with the coupling between the macrostrain and the plus and minus tilts and hence have been omitted in order to shorten the expression. The coupling between octahedral tilts and macrostrain has been studied in some detail recently (Darlington, 1996; Darlington & Knight, 1999). For a full discussion of coupling between order parameters and macrostrain, see Salje (1990).

Possible phases in which both plus and minus tilts about the same $\langle 100 \rangle$ pseudocubic directions are present have been omitted from the discussion. There is only one report of such a structure, that of KMnF₃ below 90 K (Hidaka, 1975). Such phases will never become the most stable state if the coefficient f_{rm} is sufficiently large and positive.

Apart from a_r and a_m , the coefficients can be taken to be sensibly independent of temperature; the only soft modes involve octahedral tilting. In fact, in a number of perovskites

Table 4
Weights of condensed modes in units of $u \text{ \AA}^2$.

| Hettotype | Material | $W(R_i)$ | $W(M_i)$ | $W(X_{Aij})$ | $W(X_{Oij})$ | $W(G_{Ai})$ | $W(G_{Oi})$ | $W(H_i)$ | Ref.† | Entry |
|---------------------|--------------------------------------------------------------------|----------|----------|--------------|--------------|-------------|-------------|----------|-------|-------|
| 1 R_3 | SrTiO ₃ , 77 K | 0.0726 | | | | | | | 1 | 1 |
| | SrZrO ₃ , 1223 K | 1.6971 | | | | | | | 2 | 2 |
| 2 $R_1 = R_3$ | BaCeO ₃ , 573 K | 6.7294 | | | | 0.0586 | 0.1460 | | 3 | 3 |
| | BaCeO ₃ , 773 K | 5.2701 | | | | | | | 3 | 4 |
| 3 $R_1 = R_2 = R_3$ | LaGeO ₃ , 673 K | 4.3662 | | | | | | | 4 | 5 |
| | NaNbO ₃ , 888 K | | 0.9520 | | | | | | 5 | 6 |
| 4 M_3 | NaNbO ₃ , 878 K | | 0.8965 | | | | | | 5 | 7 |
| | No available data | | | | | | | | | |
| 5 $M_1 = M_2$ | CaCu ₃ Ti ₄ O ₁₂ | | 10.2753 | | | | | 0.2031 | 6 | 8 |
| | Tb _{0.67} Cu ₃ Ti ₄ O ₁₂ | | 9.9740 | | | | | 0.1964 | 6 | 9 |
| 6 $M_1 = M_2 = M_3$ | CaCu ₃ Mn ₄ O ₁₂ | | 9.2271 | | | | | 0.1323 | 7 | 10 |
| | Li _{0.36} WO ₃ | | 5.0358 | | | | | 0.0060 | 8 | 11 |
| 7 R_2, M_3 | Na _{0.73} WO ₃ | | 0.3953 | | | | | 0.0000 | 8 | 12 |
| | Na _{0.54} WO ₃ | | 0.3657 | | | | | 0.0000 | 8 | 13 |
| 8 $M_1 = M_2, R_3$ | NaNbO ₃ , 813 K | 0.8442 | 1.2912 | 0.0082 | 0.0012 | 0.0001 | 0.0002 | 0.0042 | 5 | 14 |
| | NaNbO ₃ , 803 K | 0.9408 | 1.1623 | 0.0808 | 0.0048 | 0.0000 | 0.0067 | 0.0013 | 5 | 15 |
| 9 $R_1 = R_3, M_2$ | SrZrO ₃ , 973 K | 3.1806 | 0.8497 | 0.4539 | 0.0063 | 0.0154 | 0.0118 | 0.0002 | 2 | 16 |
| | CaFeTi ₂ O ₆ | 4.3399 | 7.3194 | 0.3690 | 0.1987 | | 0.0508 | 0.0015 | 9 | 17 |
| 9 $R_1 = R_3, M_2$ | BaCeO ₃ , 473 K | 7.2126 | 0.5108 | 0.8058 | 0.0503 | 0.0775 | 0.1518 | 0.0002 | 3 | 18 |
| | SrZrO ₃ | 5.8137 | 1.2545 | 1.7364 | 0.0958 | 0.0471 | 0.1209 | 0.0001 | 2 | 19 |
| | LaGeO ₃ | 5.0130 | 0.4181 | 1.1826 | 0.0162 | 0.0713 | 0.1034 | 0.0002 | 4 | 20 |
| | PrFeO ₃ | 7.4537 | 1.7425 | 8.3611 | 0.2237 | 0.3453 | 0.1390 | 0.0000 | 10 | 21 |
| | NdFeO ₃ | 8.3981 | 1.9033 | 10.7150 | 0.2898 | 0.4901 | 0.1649 | 0.0000 | 10 | 22 |
| | SmFeO ₃ | 9.6041 | 2.3606 | 15.1215 | 0.4215 | 0.7547 | 0.1970 | 0.0005 | 10 | 23 |
| | EuFeO ₃ | 10.0301 | 2.5231 | 17.2613 | 0.5149 | 0.9157 | 0.2237 | 0.0000 | 10 | 24 |
| | GdFeO ₃ | 10.2814 | 2.6910 | 19.5499 | 0.5419 | 1.0893 | 0.2683 | 0.0000 | 10 | 25 |
| | TbFeO ₃ | 11.1054 | 2.7621 | 20.4797 | 0.6507 | 1.1498 | 0.2368 | 0.0000 | 8 | 26 |
| | DyFeO ₃ | 11.5369 | 2.9724 | 22.5061 | 0.7089 | 1.3311 | 0.2471 | 0.0002 | 8 | 27 |
| | HoFeO ₃ | 12.0370 | 3.0026 | 23.8465 | 0.7804 | 1.4574 | 0.2704 | 0.0002 | 10 | 28 |
| | ErFeO ₃ | 12.8142 | 3.1006 | 24.9061 | 0.8218 | 1.5771 | 0.3205 | 0.0000 | 10 | 29 |
| | TmFeO ₃ | 13.1795 | 3.0947 | 25.1013 | 0.9675 | 1.6745 | 0.2982 | 0.0000 | 10 | 30 |
| | YbFeO ₃ | 13.6153 | 3.2967 | 26.7549 | 1.0592 | 1.7761 | 0.3007 | 0.0000 | 10 | 31 |
| | LuFeO ₃ | 14.3837 | 3.2072 | 27.5146 | 1.0463 | 1.8962 | 0.2892 | 0.0000 | 10 | 32 |

† References: (1) Unoki & Sakudo (1967); (2) Kennedy *et al.* (1999); (3) Knight (1995); (4) Howard & Kennedy (1999); (5) Darlington & Knight (1999); (6) Bochu *et al.* (1979); (7) Chenevas *et al.* (1975); (8) Wiseman & Dickens (1976); (9) Leinenweber & Parise (1995); (10) Marezio *et al.* (1970).

there is evidence that the whole branch between the R - and M -points softens (Denoyer *et al.*, 1971); that is, modes $[(\frac{1}{2} \frac{1}{2} \xi), \Delta_2]$ with $0 \leq \xi \leq \frac{1}{2}$ all have abnormally low frequencies. Experimentally it is usually found that the square of the frequency of a softening mode decreases more or less linearly with temperature, hence we set

$$a_r = a'_r(T - T_r), \quad a_m = a'_m(T - T_m).$$

Non-zero values of octahedral tilts arise as a result of a mode condensing at the R - and M -points of the Brillouin zone. These are primary order parameters.

There is no evidence that the other modes found in the hettotypes considered here become soft, hence a_g, a_h and a_x are taken to be positive at all temperatures. Non-zero values of the secondary order parameters G, H and X may occur through terms that couple them to the primary order parameters. For example, setting the first derivative of F with respect to G_i equal to zero gives

$$\begin{aligned} \partial F / \partial G_i = 0 = & a_g G_i + b_g G_i (G_j^2 + G_k^2) + c_g G_i^3 + f_{gr} G_i R_j^2 \\ & + g_{gr} G_i (R_j^2 + R_k^2). \end{aligned}$$

Therefore, either

$$G_i = 0$$

or

$$c_g G_i^2 = -a_g - b_g (G_j^2 + G_k^2) - f_{gr} R_j^2 - g_{gr} (R_j^2 + R_k^2). \quad (3)$$

c_g must be positive to produce a minimum in F for finite G_i .

Examination of the list of allowed condensed modes in Table 3 for the first three hettotypes shows that modes represented by G_1 and G_3 can only occur in hettotype 2. The Landau expansion and its application to form relationship (3) would suggest that non-zero values of G_i might be found in hettotypes 1 and 3 if present in hettotype 2, since the coefficients a_g, b_g, c_g, f_{gr} and g_{gr} are likely to have a weak temperature dependence. That is, if G_i are present in hettotype 2, then the following might be expected,

$$\begin{aligned} \text{Hettotype 1} & R_3, G_{O3}, G_{A3}, \\ \text{Hettotype 2} & R_1 = R_3, G_{O1} = G_{O3}, G_{A1} = G_{A3} \\ \text{Hettotype 3} & R_1 = R_2 = R_3, G_{O1} = G_{O2} = G_{O3}, \\ & G_{A1} = G_{A2} = G_{A3}. \end{aligned}$$

This sequence with change in temperature can be reproduced with suitable choice of the magnitudes of the coefficients in the expansion. A different choice can be made for which all G_i are zero in the three hettotypes.

The space groups allocated to hettotypes 1 and 3 do not allow finite G_i ; both $I4/mcm$ and $R\bar{3}c$ possess a single positional parameter to describe the atomic displacements (excluding the macrostrains), and therefore only a single irreducible representation is involved. Therefore, it appears that either the space groups allocated to hettotypes 1 and 3 are incorrect or, if the same Landau expansion can be used to describe transitions between hettotypes 1, 2 and 3 and the magnitudes of the coefficients do not change abruptly at a transition, then G_i are zero in hettotype 2.

A search amongst the centrosymmetric tetragonal space groups (numbers 123–142) for one that allows only [$R_3 G_{A3} G_{O3}$] to be present proved unsuccessful. $P4_2/mmc$ (131) allows three modes, [$G_{A3} G_{O3}$] and a mode involving oxygen displacements not considered before, $\{[(\frac{1}{2} \frac{1}{2} 0), M_4], OIII(x) = OII(y)\}$, which is an octahedral breathing mode. Tetragonal space groups exist that allow modes [$R_3 G_{A3} G_{O3}$] to be simultaneously present but also allow other modes to have finite values.

The second suggestion, *i.e.* that modes G_i are absent in hettotype 2, can be tested directly. $BaCeO_3$ shows the sequence $9:[a^-b^+a^-] \rightarrow 2:[a^-b^0a^-] \rightarrow 3:[a^-a^-a^-] \rightarrow A:[a^0a^0a^0]$ with increasing temperature (Knight, 1995). This is discussed in the following section.

Similar arguments can be applied concerning modes H_i . This mode cannot appear in $4:[a^0a^0c^+]$, and hence might be expected to be zero in $5:[a^+a^+c^0]$ and $6:[a^+a^+a^+]$. Na_xWO_3 exhibits the sequence $6:[a^+a^+a^+] \rightarrow 5:[a^+a^+c^0] \rightarrow 4:[a^0a^0c^+] \rightarrow A:[a^0a^0a^0]$ with increasing temperature (Clarke, 1977). Unfortunately, no structural determinations of hettotype 5 have been reported in the literature. Structural refinements of hettotype 6 are discussed in the following section.

A search for a centrosymmetric tetragonal space group allowing a single plus tilt and H_i modes to be present together was also unsuccessful. Space group $P4_2/mbc$ (135) allows the octahedral tilt M_3 to be present with one other mode involving oxygen displacements. The second mode is $\{[(\frac{1}{2} \frac{1}{2} \frac{1}{2}), \Gamma'_{12}], OIII(x) = -OII(y)\}$ best described as a staggered shear of the octahedra.

These arguments cannot be applied to the modes described by X_{ij} . Non-zero values of X_{ij} are only found when both plus and minus tilts are present. The space groups of hettotypes $7:[a^0b^-c^+]$, $8:[a^+a^+c^-]$ and $9:[a^-b^+a^-]$ allow all expected values of X_{ij} to be present from the coupling term $X_{ij}^2 R_j^2 M_i^2$ in the expression for F .

6. Discussion of the weights of condensed modes

The weights of condensed modes in each hettotype (apart from hettotype 5 for which there appears to be no structure refinement) are listed in Table 4. If no temperature is given in the second column, then room temperature is implied. The most commonly found hettotype is number 9. The reasons for this are discussed by Thomas & Beitollahi (1994) and by Woodward (1997b).

$BaCeO_3$ transforms from $9:[a^-b^+a^-] \rightarrow 2:[a^-b^0a^-] \rightarrow 3:[a^-a^-a^-] \rightarrow A:[a^0a^0a^0]$ with increasing temperature (Knight, 1995). The sequence provides a test of the proposition that, if the space group for hettotype 3 is correct and the Landau expansion can be applied to the sequence of transitions, G_i are zero in hettotype 2 (and possibly zero in hettotype 9 too). The fractional coordinates of the A cation in phases 9 and 2 that produce finite G_{Ai} are 0.0038 (4) and 0.0033 (4), respectively, and so appear to be real. The finite value of G_{O_i} in hettotype 2 concerns the difference in magnitude of two unrelated displacements. At 573 K, the displacements are reported as 0.3193 and 0.4296 Å. If these were exactly the same then G_{O_i} would be identically zero. The difference is outside the quoted uncertainties in fractional coordinates of the two oxygen atoms (Knight, 1995).

The rare-earth orthoferrites, [lanthanide] FeO_3 (Marezio *et al.*, 1970), indicate that both G_{Ai} and G_{O_i} are finite in hettotype 9. The weights of the condensed modes in this series increase with decrease in the radii of the A cation from 1.14 Å (Pr^{3+} , eight-coordinated) to 0.97 Å (Lu^{3+} , eight-coordinated) (Shannon & Prewitt, 1969, 1970) in a near-linear fashion.

The conclusion must be that non-zero values of G_i are finite in phases 2 and 9. Requiring G_i to be equal to zero in hettotypes 1 and 3 places restrictions on the relative magnitudes of some of the coefficients in the Landau expansion.

The situation is different concerning the coefficients involving H_i . These modes have very nearly zero weight in all reported structures analysed (including many in hettotype 9 not listed in Table 4) except for entries 8, 9 and 10 in Table 4. Note that these three materials possess two types of A cations.

Experimental results indicate that the symmetry possessed by some subsets of atoms allowed to be displaced by modes G and X are higher than required by the space group of the hettotype. $CsPbCl_3$ undergoes the sequence of transitions $4:[a^0a^0c^+] \rightarrow 7:[a^0b^-c^+] \rightarrow 9:[a^-b^+a^-]$ as the temperature decreases (Fujii *et al.*, 1974), while $CsPbBr_3$ follows the sequence $4:[a^0a^0c^+] \rightarrow 9:[a^-b^+a^-]$ (Hirotsu *et al.*, 1974). It was pointed out by both groups of workers that if a plus and a minus tilt are present in the structure then an X -point becomes a reciprocal-lattice point. Hirotsu *et al.* (1974) argued that the allowed displacements of the A cation should be described in terms of modes associated with the Z -point of the tetragonal Brillouin zone of phase $4:[a^0a^0c^+]$. However, following Cochran & Zia (1968), Darlington (1976) suggested that the displacements should be described in terms of transverse normal modes of the cubic phase. Using Cowley's table it is easy to deduce that the relevant modes at the X -point present in $7:[a^0b^-c^+]$ are described by $[(00\frac{1}{2}), M'_5]$, with potential displacements of both A and OII in the pseudocubic y direction. These have been labelled as X_{A32} and X_{O32} . The pseudocubic y component of the displacement of OII is required by the space-group symmetry to follow the pattern of displacements described by $[(00\frac{1}{2}), M'_5]$, while that of the A cation is not. There are two crystallographically distinguishable A cations in sites with the same point symmetry:

$$(0, 0, 0, \frac{1}{2}, \frac{1}{2}, 0) +$$

$$A1 \ 4cmm \ (0, y_1, \frac{1}{4})$$

$$A2 \ 4cmm \ (0, \frac{1}{2} + y_2, \frac{1}{4}).$$

The allowed displacements of these cations require modes X_{A32} and G_{A2} . Recent structural refinements of NaNbO_3 and NaTaO_3 (Darlington & Knight, 1999) indicate that within experimental error the A cations do follow the sequence of displacements described by $[(0 \ 0 \ \frac{1}{2}), M_5^-]$, that is, $y_1 = y_2$ and G_{A2} has zero weight. Constraining them to be equal does not change the quality of the fit; the value of χ^2 is essentially the same (Knight, 1999). The structures were refined from time-of-flight neutron powder diffraction patterns using the Rietveld procedure, so the constraint hardly changes the number of degrees of freedom in the refinement since the number of observations is so large. The same occurs in SrZrO_3 (Kennedy *et al.*, 1999), that is, in hettotype 7, between 970 and 1100 K, within experimental error, $y_1 = y_2$ and therefore G_{A2} has zero weight. Therefore some subsets of displacements appear to have a higher symmetry than required by the space group.

Similar effects occur in other structures. For example, the structural distortions in $\text{Sr}_3\text{Ru}_2\text{O}_7$ (Shaked *et al.*, 2000) appear to have a higher symmetry than required by the orthorhombic space group. Within the bi-layer of corner-linked octahedra, the tilts follow a minus pattern and have tetragonal symmetry, as the lattice parameters indicate. However, the topology of the structure does not allow overall fourfold symmetry and the space group must be orthorhombic.

Cox & Sleight (1979) used space group $R\bar{3}$ to refine the structure of one of the phases of $\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$ in which the valencies of the Bismuth cations are ordered. The loss of the c glide produces two distinguishable B cations (both of which are undisplaced) and hence two distinguishable octahedra; it also allows displacement of the A cations. The weights of the four modes (in units of $u \text{ \AA}^2$) in the structure at 419 K are as follows:

A cation

$$W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{15}]_x = W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{15}]_y = W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{15}]_z$$

$$= 0.0176, \quad G_{A1} = G_{A2} = G_{A3}$$

OI/OII/OIII

$$W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{25}]_x = W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{25}]_y = W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{25}]_z$$

$$= 1.2954, \quad R_1 = R_2 = R_3$$

$$W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{15}]_x = W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{15}]_y = W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma_{15}]_z$$

$$= 0.0062, \quad G_{O1} = G_{O2} = G_{O3}$$

$$W[(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), \Gamma'_2] = 0.4326, \quad \text{OI}_z = \text{OII}_y = \text{OIII}_x.$$

The last mode has not been considered before; it is a singlet at the R -point and describes a staggered 'breathing-mode' distortion of the octahedron, and has significant weight. Half the octahedra have increased volume while half have their volume decreased because of its presence. Modes described by G_{Ai} and G_{Oi} , allowed to occur in the structure, have extremely small weights; it seems likely that both are zero in this phase.

References

- Bochu, B., Deschizeaux, N. N., Joubert, J. C., Collomb, A., Chenevas, J. & Marezio, M. (1979). *J. Solid State Chem.* **29**, 291–298.
- Chenevas, J., Joubert, J. C., Marezio, M. & Bochu, B. (1975). *J. Solid State Chem.* **14**, 25–32.
- Clarke, R. (1977). *Phys. Rev. Lett.* **39**, 1550–1553.
- Cochran, W. & Zia, A. (1968). *Phys. Status Solidi*, **25**, 273–283.
- Cowley, R. A. (1964). *Phys. Rev. A*, **134**, 981–997.
- Cox, D. E. & Sleight, A. W. (1979). *Acta Cryst.* **B35**, 1–10.
- Darlington, C. N. W. (1976). *Phys. Status Solidi B*, **76**, 231–239.
- Darlington, C. N. W. (1996). *Phys. Status Solidi A*, **155**, 31–42.
- Darlington, C. N. W. & Knight, K. S. (1999). *Acta Cryst.* **B55**, 24–30.
- Denoyer, F., Comés, R. & Lambert, M. (1971). *Acta Cryst.* **A27**, 414–420.
- Fujii, Y., Hoshino, S., Yamada, Y. & Shirane, G. (1974). *Phys. Rev. B*, **9**, 4549–4559.
- Glazer, A. M. (1972). *Acta Cryst.* **B28**, 3384–3392.
- Hidaka, M. (1975). *J. Phys. Soc. Jpn*, **39**, 180–185.
- Hirotsu, S., Harada, J. & Iizumi, M. (1974). *J. Phys. Soc. Jpn*, **37**, 1393–1398.
- Howard, C. J. & Kennedy, B. J. (1999). *J. Phys. Condens. Matter*, **11**, 3229–3236.
- International Tables for Crystallography* (1992). Dordrecht: Kluwer Academic Publishers.
- Kennedy, B. J., Howard, C. J. & Chakoumakos, B. C. (1999). *Phys. Rev. B*, **59**, 4023–4027.
- Knight, K. S. (1995). *Solid State Ionics*, **75**, 109–118.
- Knight, K. S. (1999). Private communication
- Leinenweber, K. & Parise, J. (1995). *J. Solid State Chem.* **114**, 277–281.
- Marezio, M., Remeika, J. P. & Dernier, P. D. (1970). *Acta Cryst.* **B26**, 2008–2022.
- Megaw, H. D. (1973). *Crystal Structures: a Working Approach*. Philadelphia: Saunders.
- Salje, E. K. H. (1990). *Phase Transitions in Ferroelectric and Co-Elastic Crystals*. Cambridge University Press.
- Shaked, H., Jorgensen, J. D., Chmaissem, O., Ikeda, S. & Maeno, Y. (2000). *J. Solid State Chem.* **154**, 361–367.
- Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
- Shannon, R. D. & Prewitt, C. T. (1970). *Acta Cryst.* **B26**, 1046–1048.
- Thomas, N. W. & Beitollahi, A. (1994). *Acta Cryst.* **B50**, 549–560.
- Unoki, H. & Sakudo, T. (1967). *J. Phys. Soc. Jpn*, **23**, 546–552.
- Wiseman, P. J. & Dickens, P. (1976). *J. Solid State Chem.* **17**, 91–100.
- Woodward, P. M. (1997a). *Acta Cryst.* **B53**, 32–43.
- Woodward, P. M. (1997b). *Acta Cryst.* **B53**, 44–66.

Normal-mode analysis of the structures of perovskites with tilted octahedra. Erratum

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There is an error in the mode assignment for hettotype 9, $[a^-b^+a^-]$, discussed in the paper by Darlington [*Acta Cryst.* (2002). **A58**, 66–71], which has been pointed out by Dr Kevin Knight, Rutherford Appleton Laboratory, Didcot, Oxon, England. In this paper, a mode involving displacements of the anions of hettotype 9 was labelled $[(\frac{1}{2}, 0, \frac{1}{2}), M_1]$ rather than $[(\frac{1}{2}, 0, \frac{1}{2}), M_2]$. Both modes involve *plus-like* distortion of the octahedra. In the corrected Tables 1–4 shown below, this mode, which is only found in hettotype 9, has been labelled K_2 rather than H_2 . Therefore, there are not seven but eight normal modes of the cubic phase required to describe the displacements found in the nine hettotypes considered. The weights of K_2 in all the materials examined in the original paper with the structure of hettotype 9 [labelled $W(H_1)$ in the original Table 4] are correct, unaltered by the change in the labelling of the mode. It should be noted that $[(\frac{1}{2}, 0, \frac{1}{2}), M_2]$ is a longitudinal mode – the seven other modes are all transverse. The weights of K_2 are not significantly different from zero in the 15 structures examined.

References

- Bochu, B., Deschizeaux, N. N., Joubert, J. C., Collomb, A., Chenevas, J. & Marezio, M. (1979). *J. Solid State Chem.* **29**, 291–298.
- Chenevas, J., Joubert, J. C., Marezio, M. & Bochu, B. (1975). *J. Solid State Chem.* **14**, 25–32.
- Darlington, C. N. W. & Knight, K. S. (1999). *Acta Cryst.* **B55**, 24–30.
- Howard, C. J. & Kennedy, B. J. (1999). *J. Phys. Condens. Matter*, **11**, 3229–3236.
- Kennedy, B. J., Howard, C. J. & Chakoumakos, B. C. (1999). *Phys. Rev. B*, **59**, 4023–4027.
- Knight, K. S. (1995). *Solid State Ionics*, **75**, 109–118.
- Leinenweber, K. & Parise, J. (1995). *J. Solid State Chem.* **114**, 277–281.
- Marezio, M., Remeika, J. P. & Dernier, P. D. (1970). *Acta Cryst.* **B26**, 2008–2022.
- Unoki, H. & Sakudo, T. (1967). *J. Phys. Soc. Jpn.* **23**, 546–552.
- Wiseman, P. J. & Dickens, P. (1976). *J. Solid State Chem.* **17**, 91–100.

Table 1

The nine hettotypes.

| Number | +/- notation | $[M, R]$ | Multiplicity | True unit cell | Space group |
|--------|--------------|-------------------|-----------------------|-----------------------------------------|-------------------|
| 1 | $a^0a^0c^-$ | R_3 | $2 \times 2 \times 2$ | $2^{1/2} \times 2^{1/2} \times 2$ | $I4/mcm$ (140) |
| 2 | $a^-b^0a^-$ | $R_1 = R_3$ | $2 \times 2 \times 2$ | $2^{1/2} \times 2 \times 2^{1/2}$ | $Imma$ (74) |
| 3 | $a^-a^-a^-$ | $R_1 = R_2 = R_3$ | $2 \times 2 \times 2$ | $2^{1/2} \times 2^{1/2} \times 2^{1/2}$ | $R\bar{3}c$ (167) |
| 4 | $a^0a^0c^+$ | M_3 | $2 \times 2 \times 1$ | $2^{1/2} \times 2^{1/2} \times 1$ | $P4/mbm$ (127) |
| 5 | $a^+a^+c^0$ | $M_1 = M_2$ | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | $I4/mmm$ (139) |
| 6 | $a^+a^+a^+$ | $M_1 = M_2 = M_3$ | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | $Im\bar{3}$ (204) |
| 7 | $a^0b^-c^+$ | R_2, M_3 | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | $Cmcm$ (63) |
| 8 | $a^+b^-c^-$ | $M_1 = M_2, R_3$ | $2 \times 2 \times 2$ | $2 \times 2 \times 2$ | $P4_2/nmc$ (137) |
| 9 | $a^-b^+a^-$ | $R_1 = R_3, M_2$ | $2 \times 2 \times 2$ | $2^{1/2} \times 2 \times 2^{1/2}$ | $Pnma$ (62) |

Table 2

Atomic displacements in the seven normal modes, the symbol used in the construction of the Landau potential, and character of each mode.

| Normal mode | Displacement | Symbol | Character |
|--------------------------------------------------------|-------------------|-----------|-----------------------------|
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{25}$ | OI(y) = -OII(z) | R_1 | Octahedral minus tilt |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{25}$ | OI(x) = -OIII(z) | R_2 | Octahedral minus tilt |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{25}$ | OII(x) = -OIII(y) | R_3 | Octahedral minus tilt |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | OI(y) = OII(z) | G_{O1} | Octahedral minus distortion |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | OI(x) = OIII(z) | G_{O2} | Octahedral minus distortion |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | OII(x) = OIII(y) | G_{O3} | Octahedral minus distortion |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | A(x) | G_{A1} | A cation displacement |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | A(y) | G_{A2} | A cation displacement |
| $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \Gamma_{15}$ | A(z) | G_{A3} | A cation displacement |
| $(0, \frac{1}{2}, \frac{1}{2}), M_3$ | OI(y) = -OII(z) | M_1 | Octahedral plus tilt |
| $(\frac{1}{2}, 0, \frac{1}{2}), M_3$ | OI(x) = -OIII(z) | M_2 | Octahedral plus tilt |
| $(\frac{1}{2}, \frac{1}{2}, 0), M_3$ | OII(x) = -OIII(y) | M_3 | Octahedral plus tilt |
| $(0, \frac{1}{2}, \frac{1}{2}), M_1$ | OI(y) = OII(z) | H_1 | Octahedral plus distortion |
| $(\frac{1}{2}, 0, \frac{1}{2}), M_1$ | OI(x) = OIII(z) | H_2 | Octahedral plus distortion |
| $(\frac{1}{2}, \frac{1}{2}, 0), M_1$ | OII(x) = OIII(y) | H_3 | Octahedral plus distortion |
| $(0, \frac{1}{2}, \frac{1}{2}), M_2$ | OII(y) = -OI(z) | K_1 | Octahedral plus distortion |
| $(\frac{1}{2}, 0, \frac{1}{2}), M_2$ | OI(z) = -OIII(x) | K_2 | Octahedral plus distortion |
| $(\frac{1}{2}, \frac{1}{2}, 0), M_2$ | OIII(x) = -OII(y) | K_3 | Octahedral plus distortion |
| $(\frac{1}{2}, 0, 0), M_5'$ | OIII(y) | X_{O12} | Octahedral distortion |
| $(\frac{1}{2}, 0, 0), M_5'$ | OIII(z) | X_{O13} | Octahedral distortion |
| $(0, \frac{1}{2}, 0), M_5'$ | OII(z) | X_{O23} | Octahedral distortion |
| $(0, \frac{1}{2}, 0), M_5'$ | OII(x) | X_{O21} | Octahedral distortion |
| $(0, 0, \frac{1}{2}), M_5'$ | OI(x) | X_{O31} | Octahedral distortion |
| $(0, 0, \frac{1}{2}), M_5'$ | OI(y) | X_{O32} | Octahedral distortion |
| $(\frac{1}{2}, 0, 0), M_5'$ | A(y) | X_{A12} | Cation displacement |
| $(\frac{1}{2}, 0, 0), M_5'$ | A(z) | X_{A13} | Cation displacement |
| $(0, \frac{1}{2}, 0), M_5'$ | A(z) | X_{A23} | Cation displacement |
| $(0, \frac{1}{2}, 0), M_5'$ | A(x) | X_{A21} | Cation displacement |
| $(0, 0, \frac{1}{2}), M_5'$ | A(x) | X_{A31} | Cation displacement |
| $(0, 0, \frac{1}{2}), M_5'$ | A(y) | X_{A32} | Cation displacement |

addenda and errata

Table 3

The space group, possible condensed modes and non-zero pseudocubic spontaneous macrostrain in the nine hettotypes.

| Number | Space group | Allowed modes | Macrostrain |
|--------|-------------------|-----------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| 1 | $I4/mcm$ (140) | R_3 | $\varepsilon_{11} = \varepsilon_{22}; \varepsilon_{33}$ |
| 2 | $Imma$ (74) | $R_1 = R_3$ $G_{O1} = G_{O3}$ $G_{A1} = G_{A3}$ | $\varepsilon_{11} = \varepsilon_{33}; \varepsilon_{22}; \varepsilon_{31}$ |
| 3 | $R\bar{3}c$ (167) | $R_1 = R_2 = R_3$ | $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}; \varepsilon_{23} = \varepsilon_{31} = \varepsilon_{12}$ |
| 4 | $P4/mbm$ (127) | M_3 | $\varepsilon_{11} = \varepsilon_{22}; \varepsilon_{33}$ |
| 5 | $I4/mmm$ (139) | $M_1 = M_2$ | $\varepsilon_{11} = \varepsilon_{22}; \varepsilon_{33}$ |
| 6 | $Im\bar{3}$ (204) | $H_1 = H_2 \neq H_3$ $M_1 = M_2 = M_3$ $H_1 = H_2 = H_3$ | $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{33}$ |
| 7 | $Cmcm$ (63) | R_2 M_3 G_{O2} G_{A2} H_3 X_{O32} X_{A32} | $\varepsilon_{11}; \varepsilon_{22}; \varepsilon_{33}$ |
| 8 | $P4_2/nmc$ (137) | R_3 $M_1 = M_2$ G_{O3} $H_1 = H_2$ $X_{O13} = X_{O23}$ $X_{A13} = X_{A23}$ | $\varepsilon_{11} = \varepsilon_{22}; \varepsilon_{33}$ |
| 9 | $Pnma$ (62) | $R_1 = R_3$ M_2 $G_{O1} = G_{O3}$ $G_{A1} = G_{A3}$ K_2 $X_{O21} = X_{O23}$ $X_{A21} = X_{A23}$ | $\varepsilon_{11} = \varepsilon_{33}; \varepsilon_{22}; \varepsilon_{31}$ |

Table 4

Weights of condensed modes in units of $u \text{ \AA}^2$.

| Hettotype | Material | $W(R_i)$ | $W(M_i)$ | $W(X_{Aij})$ | $W(X_{Oij})$ | $W(G_{Ai})$ | $W(G_{Oi})$ | $W(H_i)$ | $W(K_i)$ | Ref.† | Entry |
|---------------------|--------------------------------------------------------------------|----------|----------|--------------|--------------|-------------|-------------|----------|----------|-------|-------|
| 1 R_3 | SrTiO ₃ , 77 K | 0.0726 | | | | | | | | 1 | 1 |
| | SrZrO ₃ , 1223 K | 1.6971 | | | | | | | | 2 | 2 |
| 2 $R_1 = R_3$ | BaCeO ₃ , 573 K | 6.7294 | | | | 0.0586 | 0.1460 | | | 3 | 3 |
| 3 $R_1 = R_2 = R_3$ | BaCeO ₃ , 773 K | 5.2701 | | | | | | | | 3 | 4 |
| | LaGeO ₃ , 673 K | 4.3662 | | | | | | | | 4 | 5 |
| 4 M_3 | NaNbO ₃ , 888 K | | 0.9520 | | | | | | | 5 | 6 |
| | NaTaO ₃ , 878 K | | 0.8965 | | | | | | | 5 | 7 |
| 5 $M_1 = M_2$ | No available data | | | | | | | | | | |
| 6 $M_1 = M_2 = M_3$ | CaCu ₃ Ti ₄ O ₁₂ | | 10.2753 | | | | | 0.2031 | | 6 | 8 |
| | Tb _{0.67} Cu ₂ Ti ₄ O ₁₂ | | 9.9740 | | | | | 0.1964 | | 6 | 9 |
| | CaCu ₃ Mn ₄ O ₁₂ | | 9.2271 | | | | | 0.1323 | | 7 | 10 |
| | Li _{0.36} WO ₃ | | 5.0358 | | | | | 0.0060 | | 8 | 11 |
| | Na _{0.73} WO ₃ | | 0.3953 | | | | | 0.0000 | | 8 | 12 |
| | Na _{0.54} WO ₃ | | 0.3657 | | | | | 0.0000 | | 8 | 13 |
| 7 R_2, M_3 | NaNbO ₃ , 813 K | 0.8442 | 1.2912 | 0.0082 | 0.0012 | 0.0001 | 0.0002 | 0.0042 | | 5 | 14 |
| | NaTaO ₃ , 803 K | 0.9408 | 1.1623 | 0.0808 | 0.0048 | 0.0000 | 0.0067 | 0.0013 | | 5 | 15 |
| | SrZrO ₃ , 973 K | 3.1806 | 0.8497 | 0.4539 | 0.0063 | 0.0154 | 0.0118 | 0.0002 | | 2 | 16 |
| 8 $M_1 = M_2, R_3$ | CaFeTi ₂ O ₆ | 4.3399 | 7.3194 | 0.3690 | 0.1987 | | 0.0508 | 0.0015 | | 9 | 17 |
| 9 $R_1 = R_3, M_2$ | BaCeO ₃ , 473 K | 7.2126 | 0.5108 | 0.8058 | 0.0503 | 0.0775 | 0.1518 | | 0.0002 | 3 | 18 |
| | SrZrO ₃ | 5.8137 | 1.2545 | 1.7364 | 0.0958 | 0.0471 | 0.1209 | | 0.0001 | 2 | 19 |
| | LaGeO ₃ | 5.0130 | 0.4181 | 1.1826 | 0.0162 | 0.0713 | 0.1034 | | 0.0002 | 4 | 20 |
| | PrFeO ₃ | 7.4537 | 1.7425 | 8.3611 | 0.2237 | 0.3453 | 0.1390 | | 0.0000 | 10 | 21 |
| | NdFeO ₃ | 8.3981 | 1.9033 | 10.7150 | 0.2898 | 0.4901 | 0.1649 | | 0.0000 | 10 | 22 |
| | SmFeO ₃ | 9.6041 | 2.3606 | 15.1215 | 0.4215 | 0.7547 | 0.1970 | | 0.0005 | 10 | 23 |
| | EuFeO ₃ | 10.0301 | 2.5231 | 17.2613 | 0.5149 | 0.9157 | 0.2237 | | 0.0000 | 10 | 24 |
| | GdFeO ₃ | 10.2814 | 2.6910 | 19.5499 | 0.5419 | 1.0893 | 0.2683 | | 0.0000 | 10 | 25 |
| | TbFeO ₃ | 11.1054 | 2.7621 | 20.4797 | 0.6507 | 1.1498 | 0.2368 | | 0.0000 | 8 | 26 |
| | DyFeO ₃ | 11.5369 | 2.9724 | 22.5061 | 0.7089 | 1.3311 | 0.2471 | | 0.0002 | 8 | 27 |
| | HoFeO ₃ | 12.0370 | 3.0026 | 23.8465 | 0.7804 | 1.4574 | 0.2704 | | 0.0002 | 10 | 28 |
| | ErFeO ₃ | 12.8142 | 3.1006 | 24.9061 | 0.8218 | 1.5771 | 0.3205 | | 0.0000 | 10 | 29 |
| | TmFeO ₃ | 13.1795 | 3.0947 | 25.1013 | 0.9675 | 1.6745 | 0.2982 | | 0.0000 | 10 | 30 |
| | YbFeO ₃ | 13.6153 | 3.2967 | 26.7549 | 1.0592 | 1.7761 | 0.3007 | | 0.0000 | 10 | 31 |
| | LuFeO ₃ | 14.3837 | 3.2072 | 27.5146 | 1.0463 | 1.8962 | 0.2892 | | 0.0000 | 10 | 32 |

† References: (1) Unoki & Sakudo (1967); (2) Kennedy *et al.* (1999); (3) Knight (1995); (4) Howard & Kennedy (1999); (5) Darlington & Knight (1999); (6) Bochu *et al.* (1979); (7) Chenevas *et al.* (1975); (8) Wiseman & Dickens (1976); (9) Leinenweber & Parise (1995); (10) Marezio *et al.* (1970).